

Role of Mixed Catalysts in Composite Solid Rocket Propellant Combustion

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(Received on: July 30, 2013)

ABSTRACT

In an attempt to elucidate the site of action of combustion catalysts in augmenting burning rates of composite solid rocket propellants based on Carboxyl terminated Polybutadiene (CTPB)–Ammonium per chlorate (AP), efforts have been made to understand the role of n-butylferrocene (n-BFC), copper chromite (CC), and mixed catalyst system of n-BFC. In respect of copper chromite, at higher catalyst concentrations, diffusion mixing parameters are more dominating than the reaction controlling parameters, and the reverse is true at lower concentrations. Further, with increase in concentration, the pressure exponent also increases indicating the sensitivity of the composition. In the case of n-butylferrocene catalyzed propellant system, both the reaction time parameters and the pressure exponent values remain steady and, with increasing in concentration of n-butyl ferrocene, the diffusion mixing parameter decreases indicating that it is the process that is rate controlling. Interestingly, in the mixed catalyst system, the reverse phenomenon is observed where it is the reaction controlled processes are the dominating ones.

Keywords: Ferrocene, n-butylferrocene, Copper Chromite, burning rate, diffusion controlled, reaction controlled, Carboxyl terminated polybutadiene, ammonium, per chlorate.

1. INTRODUCTION

Controversy still persists over the site of action of catalysts in composite solid propellant combustion. They may act in the condensed-phase decomposition of the

oxidizer and fuel-binder molecules; or in the gas-phase reaction of the oxidizer and binder pyrolysis products, and/or a heterogeneous surface catalysis role to promote the combustion reactions. Earlier studies¹ with catalyzed propellants covering a range of fuels and oxidizers suggested that catalysts act by promoting the decomposition of perchloric acid resulting from the thermal decomposition of ammonium per chlorate, an oxidizer widely employed in composite solid rocket propellant formulations. Charles U. Pittman Jr.² suggests that catalysts act by catalyzing the decomposition of HClO_4 or its immediate decomposition products in the gas-phase. Coates³ concluded that catalysts increased the HClO_4 reaction with NH_3 by promoting HClO_4 decomposition in studies of rapid propellant pyrolysis in a mass spectrometer.

In the present investigation, we have studied the effect of n-butylferrocene, copper chromite, and mixed catalyst system of n-butylferrocene with copper chromite, and tried to understand the role played by the reaction controlled and diffusion controlled processes in modifying the combustion rates of composite solid rocket

propellants, based on carboxyl terminated polybutadiene (CTPB) and ammonium per chlorate (AP).

2. EXPERIMENTAL

Ammonium per chlorate was procured from M/s. WIMCO, Mumbai. The CTPB polymer was procured from M/s. B. F. Goodrich Chemical Co., USA. The aluminum powder used was procured from M/s. Metal Powder Factory, Madurai. Copper Chromite catalyst used was an in-house prepared one. N-butylferrocene was procured from M/s. Research Organic/Inorganic Chemical Corporation, West Coast, 1686, Sheldon St., California.

The propellant formulation was an 84 percent solid loading one. The Coarse to fine oxidizer ratio was maintained at 2:1. The catalyst concentration varied from 'zero' to 'two' percent by weight of the propellant formulation. The propellant was plasticized with a mineral oil and cured with MAPO system. Burning rate measurements were done in a conventional Crawford Bomb⁴ under nitrogen gas pressure, pressure ranging between 30 – 70 Kg. Cm^{-2} .

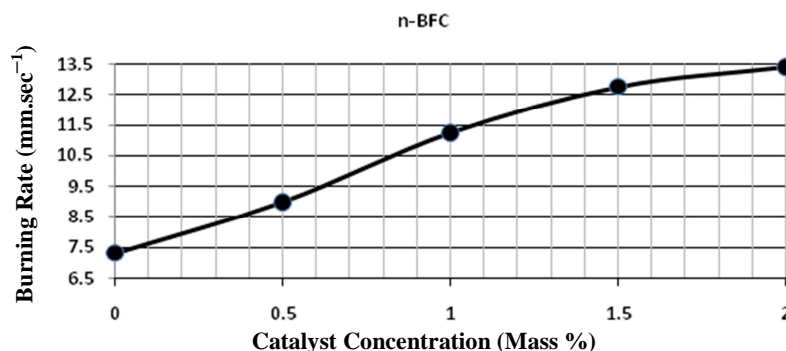


Fig.1. n-Butyl Ferrocene Concentration vs. Propellant, Burning Rate at 70 KSC

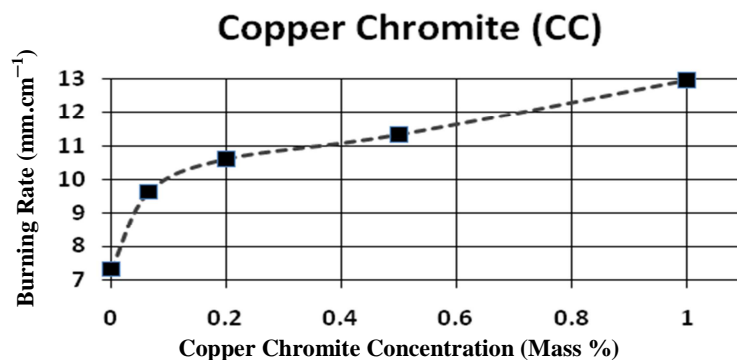


Fig.2. Copper Chromite Concentration vs. Propellant, Burning Rate at 70 KSC

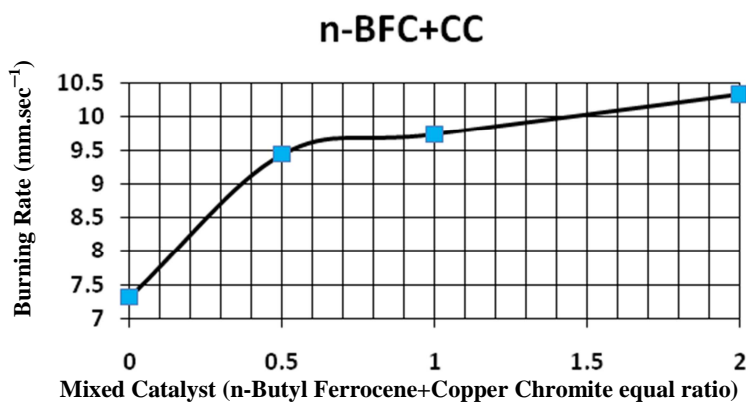


Fig.3. Mixed Catalyst Concentration vs. Propellant, Burning Rate at 70 KSC

Table-1: Summerfield's Burning Rate Equation Parameters for both Catalyzed and Non-catalyzed Propellant Systems

Catalyst	Concentration (Mass %)	Summerfield's Burning Rate Equation Parameters	
		a'	b
Uncatalyzed	0	15.64	4.75
n-butyl ferrocene	1.0	7.6	3.25
n-butyl ferrocene	1.5	7.68	2.79
n-butyl ferrocene	2.0	7.6	2.64
Copper Chromite	0.2	14.20	3.10
Copper Chromite	0.5	14.55	2.83
Copper Chromite	1.0	15.60	2.3
n-BFC + CC	0.25/0.25	15.13	3.51
n-BFC + CC	0.50/0.50	11.06	3..62
n-BFC + CC	1.0/1.0	5.09	3.72

3. RESULTS AND DISCUSSION

The burning rates at 70 KSC as a function of catalyst concentration for unanalyzed propellant, and those catalyzed with n-butyl ferrocene, copper chromite, copper acetylacetonate, n-butyl ferrocene +

copper chromite system are presented in Fig.1 to Fig. 3.

The Summerfield's burning rate equation parameters⁵ for these propellant systems are given in Table-1. The parameter 'a' represents the reaction time parameter, and 'b' represents the diffusional mixing aspect of the combustion reaction.

Table-2: Catalyzed to uncatalyzed Burning Rate Ratio at 70 KSC of AP-CTPB based ropellants catalyzed with n-Butyl Ferrocene, Copper Chromite, n-butyl ferrocene + Copper Chromite

Catalyst	Catalyst Concentration	Catalyzed / Uncatalyzed Burning Rate Ratio at 70 KSC
Uncatalyzed	0	--
n-butyl ferrocene	0.5	1.23
n-butyl ferrocene	1.0	1.53
n-butyl ferrocene	1.5	1.74
n-butyl ferrocene	2.0	1.83
Copper Chromite	0.065	1.32
Copper Chromite	0.2	1.45
Copper Chromite	0.5	1.55
Copper Chromite	1.0	1.77
n-BFC + CC	0.25/0.25	1.29
n-BFC + CC	0.50/0.50	1.33
n-BFC + CC	1.0/1.0	1.41

Note: Uncatalyzed propellant burning rate at 70KSC is 7.32 mm/sec.

From Table-1, it can be seen that, in the case of copper chromite, with increase in catalyst concentration, the reaction time parameter increases from a slightly lower value than the uncatalyzed composition and approaching to that of uncatalyzed one; while the diffusion time parameter decreases. In the case of n-butyl ferrocene, the reaction time parameter becomes just half of the uncatalyzed propellant system at 1.0 percent by mass of the catalyst and then on increases in catalyst concentration has no influence on the reaction time parameter;

while the diffusional mixing parameter is lowered with increase in concentration of the catalyst.

Coming to the mixed catalyst system, at lower concentrations of the mixed catalyst, the reaction time parameter is closer to that of the uncatalyzed composition and gradually decreases with the increase in the mixed catalyst concentration and just becomes one-third at 1:1 ratio. At the same time, there is a small decrease in the diffusion time parameter which more or less remains constant with increase in

concentration of the mixed catalyst. It means that, at 1:1 ratio of the mixed catalyst system one can expect a good reaction time with a steady diffusional mixing taking place which can lead to stable combustion of the propellant. Moreover, with this composition of the catalyst, since n-butyl ferrocene is not only acts as a combustion rate modifier but also acts as a plasticizer to the propellant system. It helps in the processing of the propellant by improving the fluidity of the system.

The propellants under this study can be graded on the basis of the catalyzed to uncatalyzed burning rate ratio when their burning rates at 70 KSC are compared. This information is presented in Table-2.

CONCLUSIONS

n-butyl ferrocene at concentrations beyond 1.5 percent by mass appears to be a better catalyst than copper chromite. It can also act as a plasticizer and hence a part of the inert plasticizer from the propellant formulation can be replaced with it. At 2 percent level, both the reaction time parameter and diffusion time parameter are considerably low and hence there is a good scope for attaining stable combustion of the propellant system. Moreover, n-butyl ferrocene is supposed to decompose in the gas-phase leading to in-situ formation of

nano-dimensional iron oxide in the gas-phase providing for better catalysis.

Coming to the mixed catalyst system, the composition of 1.0:1.0 gives the same performance as that of 0.20 percent copper chromite composition, but, with better reaction time and diffusion time parameter values. This leads to fewer solids in the gas plume thereby increasing the velocity of the exhaust gases.

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